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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: REINFORCED POLYMER COMPOSITION

(57) Abstract: A partially cured reinforced polymeric article which includes one or more layers, each layer including: a reinforcing web; a partially cured cross-linkable polymeric composition being formed from: an ultra-violet (UV) curable polymeric resin; and a photoinitiator; or a photoinitiator and a thermal initiator wherein the polymeric resin and photoinitiator are selected to permit formation of the partially cured cross-linkable polymeric composition in less than approximately 120 seconds.

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REINFORCED POLYMER COMPOSITION

The present invention relates to a cross-linkable polymeric fibre coating composition and method of preparing same. The invention also relates to articles formed using this process.

5 Continuous fibre reinforced polymer matrix materials (hereinafter referred to as "reinforced polymer materials") are used for numerous flat and curved panel applications in the aerospace/aeromotive, industrial, chemical, building and sporting goods industries.

Traditionally, reinforced polymer materials are manufactured by the "lay-up" method. Fibres are laid over the mould and the polymer resin is poured and worked into the fibres, and cured *in situ*. The two most common and serious material defects in reinforced polymer materials are (i) poor wetting of the fibre by the resin with appearance of voids in the polymer matrix, and (ii) excessive wetting of the fibre with resin rich pocket creation. Both of these defects can prevent the material from reaching its maximum potential in mechanical properties and can cause premature failure of the material when in use. The lay-up method is unsuitable for achieving maximum mechanical properties in a consistent and reliable manner.

Partially cured reinforced polymer composites (hereinafter referred to as "prepregs" were developed in an attempt to overcome some of the disadvantages associated with reinforced polymer materials made according to the lay-up method. Prepregs are used generally for applications in specialist areas such as the aerospace industry.

The term "prepreg" as used herein refers to a partially cured article which comprises a reinforcing web or other such substrate impregnated with a polymeric matrix composition. The composite can be in rod, rope, fibre, roving, strand, tow, sheet or other form. A reinforcing sheet is preferred.

The "prepregging" method has been used in the prior art, for example in the

aerospace industry, to (i) maximise the strength and stiffness of the materials, (ii) minimise the material defects of the materials, and (iii) to create material suitable for temporary storage and easy use. Prepreg materials may also be produced with consistent mechanical properties.

5 The prepregging method involves impregnating fibres (in a uniaxial or multiaxial continuous fabric form) with liquid resin in a manner that controls precisely the fibre-resin volume composition. The liquid resin may be partially cured, so that the resin becomes gel-like (ie: more viscous), but retains its adhesive and reactive properties. The process of partially curing the resin material
10 is known as "B-staging".

Multiple prepregs can then be consolidated into a shaped article.

Accordingly, it is the object of this invention to overcome, or at least alleviate one or more of the difficulties, and/or deficiencies, related to the prior art.

In a first aspect, there is provided a partially cured reinforced polymeric
15 article which includes one or more layers, each layer including:

a reinforcing web;

a partially cured cross-linkable polymeric composition being formed
from:

an ultra-violet (UV) curable polymeric resin; and

20 a photoinitiator; or

a photoinitiator and a thermal initiator

wherein the polymeric resin and photoinitiator are selected to permit formation of the partially cured cross-linkable polymeric composition in less than approximately 120 seconds.

25 The applicants have surprisingly found that by partially curing the composition in a first stage, a reinforced polymeric article may be prepared very

rapidly, e.g. in a matter of seconds. This article may then be stored for an extended period in a suitable manner, and later used and shaped as required, before conducting the final UV and/or thermal cure of the composition.

Preferably, the partially cured cross-linkable polymeric composition is
5 formed in approximately 5 to 60 seconds, more preferably in approximately 10 to 45 seconds.

The reinforcing web may be impregnated with the partially cured cross-linkable polymeric composition.

The polymeric article may include two or more layers. The layers may be of
10 substantially the same thickness. Alternatively, one or more of the layers may be of differing thickness from one other layer in the article.

One or more layers in the article may include a reinforcing web of differing material from the reinforcing web of one other layer in the article. For example, the article may include alternating layers of glass fibre and carbon fibre.

15 The partially cured reinforced polymeric article remains in a pliable state so may be folded, or preferably rolled, for ease of storage and transportation, as discussed below.

Preferably, the partially cured reinforced polymeric article has a weight of from approximately 20 to 2000 g/m², preferably approximately 100 to 1500 g/m²,
20 more preferably 500 to 1000 g/m².

All types of fibre reinforcements or other reinforcing materials commonly used for these applications may be used as the reinforced web. Examples include, but are not limited to, one or more of glass fibres, carbon and graphite fibres, polymeric fibres (including aramide fibres), boron filaments, ceramic fibres, metal
25 fibres, asbestos fibres, beryllium fibres, silica fibres and silicon carbide fibres. Glass fibres, in the form of fibreglass sheets or matts are preferred.

The UV curable polymeric resin material may include a curable polyester or

vinyl ester resin. An epoxy vinyl ester resin is preferred. A bisphenol-A epoxy resin is particularly preferred. Examples include, but are not limited to, the Nuplex family of resins (polyester resins), and the Derakane family of resins (epoxy vinyl esters) (available from The Dow Chemical Company).

- 5 As stated above, the partial curing of the polymeric article is achieved by UV radiation.

Any commercially viable UV curing system may be used.

- 10 The photoinitiator may be present in any suitable amount to provide the desired level of curing. The amount of initiation may vary depending on the polyester or vinyl ester resin used. Preferably, the photoinitiator is present in an amount from 0.01% to 5% by weight. Most preferably, the photoinitiator is present in an amount from 0.1% to 2% by weight.

- 15 Examples of photoinitiators which may be used in the present process include, but are not limited to Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-{4-(methylthio)phenyl}-2-morpholino-propanone-1, Merck Darocur 1664, Rohm Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55 (55) (methyl phenyl glyoxylate phenyl ketone).

- 20 Examples of thermal initiators which may be used in the present process include, but are not limited to peroxides including benzoyl peroxide (BPO), cumene hydro peroxide (CHP), 1,1-di-*tert*-butyl peroxy-3,3,5-trimethylcyclohexane, and *sec*-isopropyl percarbonate.

- 25 The initiator may include a single component, or a combination of initiator components.

Other additives or modifiers may be present which are conventionally used in resin compositions. Such additives or modifiers may include: inhibitors, UV stabilisers, UV absorbers, antioxidants, tinting agents, transfer agents, viscosity

modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers, thixotropic agents, slip and blocking agents, and air release agents.

Accordingly, a further aspect of the present invention relates to a process
5 for preparing a partially cured reinforced polymeric article including:

providing one or more layers, each layer including:

a reinforcing web; and

an effective amount of a cross-linkable polymeric composition
including:

10 a UV curable polymeric resin and

a photoinitiator; or

a photoinitiator and a thermal initiator;

impregnating the reinforcing web with the cross-linkable polymeric
composition; and

15 exposing the impregnated web to a source of ultraviolet (UV)
radiation for a period of less than approximately 120 seconds, at an intensity
sufficient to partially cure the resin.

Preferably, the partially cured cross-linkable polymeric composition is
formed in approximately 5 to 60 seconds, more preferably in approximately 10 to
20 45 seconds.

The partial UV curing of the resin material may be achieved with exposure of
the prepreg to UV light with an intensity of from approximately 1×10^{-5} to 10×10^{-7}
 W/cm^2 . More preferably, the intensity of the UV light is between 5×10^{-5} and $5 \times$
 10^{-6} W/cm^2 .

25 The partial UV curing of the resin material may be achieved with exposure of
the prepreg to UV light for a time sufficient to achieve a desired level of curing.
The exposure time is dependent on the light intensity selected but generally will

extend from approximately 1 to 120 seconds, more preferably approximately 5 to 60 seconds, most preferably approximately 10 to 45 seconds.

It will be understood that the time of manufacture is accordingly very significantly reduced relative to prior art hand layering methods.

- 5 Preferably, the ratio of resin material to fibre material is between approximately 10 and 90% by weight.

More preferably, the ratio of resin material to fibre material is from 25 to 75%, more preferably by 35 to 65% by weight.

- Once the prepregs have been partially cured, they are able to be stored.
- 10 The prepregs may be stored indefinitely for periods up to 1 year when stored in a suitable manner (eg; prevented from exposure to UV light).

As discussed, the partially cured reinforced polymeric article is pliable and may be folded or rolled or otherwise packaged for ease of storage.

- As the reinforced polymeric article preferably exhibits a significant degree of tack, one or more surfaces of the article may be provided with a protective layer, both to permit rolling and to avoid contamination with dust and the like during storage.
- 15

- Accordingly, in a further aspect of the present invention there is provided a laminate polymeric article including
- 20 a partially cured reinforced polymeric article as described above; and
- a first protective coating or film overlaying at least a portion of a surface of the reinforced polymeric article.

- The first protective coating or layer may be of any suitable material. A polymeric film or sheet may be used. A thermoplastic polymeric film such as a polyethylene, polypropylene or nylon film is preferred.
- 25

Where the reinforced polymeric article forms a sheet or film, the protective

coating or layer may be applied to one, or preferably both, major surfaces thereof.

In a preferred embodiment of this aspect of the present invention, the partially cured reinforced polymer article may be provided with a protective coating or layer which is UV opaque. This may provide further protection against
5 premature final cure.

The UV opaque protective coating may be provided by the first protective layer described above. However, preferably the UV opaque protective coating is a supplementary coating.

Accordingly, in a preferred embodiment, the laminated polymeric article
10 further includes

a UV opaque outer coating overlaying at least in part an exposed surface of the partially cured reinforced polymeric article or first protective coating or film.

For example, where the partially cured reinforced polymeric article is provided in a rolled form, the UV opaque outer coating may constitute an outer
15 sheath or sleeve thereover.

The UV opaque outer coating may be of any suitable type. A metal material, such as an aluminium foil, may be used. A metal foil is preferred as it is both light and gas impervious and may, in addition, reduce or eliminate loss of volatiles from the partially cured polymeric material.

20 In a further aspect of the present invention, when required to be used, the partially cured polymeric article according to the present invention may be formed into a shaped article. The shaped article may then be subjected to a final curing step. The final cure may be achieved by UV radiation or heat.

Accordingly, in a further aspect of the present invention there is provided a
25 process of forming a shaped article including:

shaping one or more partially cured reinforced polymeric articles (as described above) into a desired form; and
subjecting the formed article to a final curing step.

In a preferred form of the present invention, a final cure may include a UV curing step.

Accordingly the process according to this aspect of the present invention may further include exposing the formed article to a source of UV radiation for a
5 period, and at an intensity, sufficient to achieve final cure.

When the resin system is formulated with a photoinitiator only, the final cure may be achieved through further exposure to UV light. The UV light intensity and exposure time is much greater than that used for the partial curing (or B-staging) step.

10 When the complete or final curing of the resin is achieved through a UV cure, the prepregs have a long shelf life, provided they are protected from further incidental UV exposure.

When the resin system is formulated with a photoinitiator and a thermal initiator, the final cure may be achieved at room temperature with exposure to a
15 UV source, or preferably through use of an autoclave or other system which can apply heat and pressure to the composite laminate and provide a more rapid cure.

The intensity and duration of final cure is also dependent on the number of the partially cured reinforced articles (prepregs) utilised in forming the final shaped article. Whilst the relationships are not directly proportional, in general, as the
20 number of layers increases, the intensity and/or duration increases.

The final UV curing of the resin material may be achieved with exposure of the prepreg to UV light with an intensity of from approximately 1×10^{-4} to 1×10^{-6} W/cm². More preferably, the intensity of the UV light is between approximately 5×10^{-4} and 5×10^{-5} W/cm².

25 The final UV curing of the resin material may be achieved with exposure of the prepreg a source of UV radiation for a time of from approximately 0.5 to 120 minutes. Preferably, the UV exposure is from approximately 1 minute to 60 minutes. More preferably, the UV exposure time is from approximately 10 to 45

minutes.

The final UV curing time depends on the number of layers to be cured and the resin/fibre ratio.

In an alternative embodiment, the final curing step may be, or include, a
5 thermal curing.

The process according to this aspect of the present invention includes
subjecting the formed article to a final curing step including applying heat to
the shaped article at a temperature and for a period sufficient to achieve a final
cure.

10 Preferably, the temperature of the final cure occurs at a temperature of
between approximately 50 and 150°C. More preferably, the temperature is
between approximately 65 and 100°C.

The final cure may be achieved with exposure of the formed article to heat
for a time from approximately 30 minutes to 4 hours. The exposure time required
15 depends on the curing temperature and the resin/fibre ratio.

Preferably, the pressure applied during the final cure is between
approximately 30 and 100 psi. More preferably, the pressure is between 50 and
70 psi.

The thermal curing may be achieved using any suitable heat source. For
20 example, the heat source may include, but is not limited to a heated press, a
heated oven, a heated mould, and the like.

In a further aspect of the present invention there is provided a cured shaped
article formed as described above.

The present invention will now be more fully described with reference to the
25 accompanying examples. The examples describe UV B-staging for a number of
systems with different fibre and resin combinations, and for two different UV B-

staging processes.

It should be understood that the description following is illustrative only and should not be taken in any way as a restriction on the generality of the invention described above.

5

EXAMPLES

General

The tack for each prepreg was measured using a floating roller peel test based on ASTM D3167. The average force to peel the prepreg from a rigid aluminium substrate is used as the measure of tack. Increasing tack force is
10 consistent with an increase in resin mass fraction.

EXAMPLE 1

Glass/polyester prepreg for UV B-staging and UV final cure

A polyester resin (Nuplex F61042) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator. A quadraxial glass-fibre fibre fabric (1200
15 gsm) and a Twill glass-fibre fibre fabric (385 gsm) was impregnated with the liquid resin then passed under a 400 watt Mercury vapour lamp. The UV light intensity was 7×10^{-7} W/cm² and the exposure time ranged from 15 to 30 seconds.

The resin mass fraction was 35% in the Quadraxial prepreg and 50% in the Twill prepreg. The shelf life of these products is at least 6 months when protected
20 from UV exposure. The final cure is achieved through further exposure of the article to UV light of the same source and wavelength as used in the B-staging step until the curing is complete.

EXAMPLE 2

Glass/polyester prepreg for UV B-staging and UV final cure:

25 A polyester resin (Nuplex F61042) was formulated with 0.5 parts per

hundred of Irgacure 819 photoinitiator. A woven roving glass-fibre fibre fabric (635 gsm) was impregnated with the liquid resin. B-staging was done under a UVA blacklight using 2x20 watt tubes. The UV intensity in the UVA range was approximately 4.7 mW/cm^2 and the exposure time was 10 seconds.

- 5 The resin mass fraction was 50%. The shelf life of this product is at least 6 months when protected from UV exposure. The final cure is achieved through further exposure of the article to UV light of the same source and wavelength as used in the B-staging step until the curing is complete.

EXAMPLE 3

10 ***Glass/vinylester prepreg for UV B-staging and UV final cure:***

- A vinylester resin (Dow Derakane 411-350) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm^2 and the exposure time was 10 seconds.
- 15

The resin mass fraction was 50%. The shelf life of this product is at least 6 months when protected from UV exposure. The final cure is achieved through further exposure of the article to UV light of the same source and wavelength as used in the B-staging step until the curing is complete.

20

EXAMPLE 4

Glass/polyester prepreg for UV B-staging and final thermal cure:

- A polyester resin (Nuplex F61042) was formulated with 0.5 parts per hundred (pph) of Irgacure 819 photoinitiator, and 4 pph benzoyl peroxide (BPO) or 1 pph cumene hydro peroxide (CHP) thermal catalysts. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm^2 and the exposure time was 10 seconds.
- 25

The shelf life of this product at room temperature is limited due to the presence of the thermal catalyst in the resin formulation. It must also be protected from UV exposure when stored. Final cure can be achieved through further UV exposure but this is example is specifically for manufacturers who prefer a thermal
5 cure prepreg. The formulation with BPO will require 80°C for 15-20 minutes. The formulation with CHP will require 100°C for 10-15 minutes.

EXAMPLE 5

Glass/vinylester prepreg for UV B-staging and final thermal cure:

A vinylester resin (Dow Derakane 411-350) was formulated with 0.5 parts
10 per hundred of Irgacure 819 photoinitiator, and 4 pph benzoyl peroxide (BPO) thermal catalyst. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm² and the exposure time was 10 seconds.

15 The shelf life of this product at room temperature is limited due to the presence of the thermal catalyst in the resin formulation. It must also be protected from UV exposure when stored. Final cure can be achieved through further UV exposure but this is example is specifically for manufacturers who prefer a thermal cure prepreg. With BPO in the formulation, a thermal cure of 80°C for
20 approximately 20 minutes is required.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the present
25 invention.

It will also be understood that the term "comprises" (or its grammatical variants) as used in this specification is equivalent to the term "includes" and should not be taken as excluding the presence of other elements or features.

CLAIMS

1. A partially cured reinforced polymeric article which includes one or more layers, each layer including:
- 5 a reinforcing web;
- a partially cured cross-linkable polymeric composition being formed from:
- an ultra-violet (UV) curable polymeric resin; and
- a photoinitiator; or
- a photoinitiator and a thermal initiator
- 10 wherein the polymeric resin and photoinitiator are selected to permit formation of the partially cured cross-linkable polymeric composition in less than approximately 120 seconds.
2. A polymeric article according to claim 1 wherein the partially cured cross-linkable polymeric composition is formed in approximately 5 to 60 seconds.
- 15 3. A polymeric article according to claim 2 wherein the partially cured cross-linkable polymeric composition is formed in approximately 10 to 45 seconds.
4. A polymeric article according to any one of claims 1 to 3 wherein there are two or more layers and the layers are of substantially the same thickness.
- 20 5. A polymeric article according to any one of claims 1 to 3 wherein there are two or more layers and one or more of the layers is of a differing thickness from one other layer in the article.
6. A polymeric article according to any one of claims 1 to 5 wherein there are two or more layers and one or more of the layers includes a reinforcing
- 25 web of differing material from the material of one other layer in the article.

7. A polymeric article according to any one of claims 1 to 6 wherein the cross-linkable polymeric composition is present in an amount between approximately 10 and 90% by weight.

8. A polymeric article according to claim 7 wherein the cross linkable
5 polymeric composition is present in an amount between approximately 25 and 75% by weight.

9. A polymeric article according to claim 8 wherein the cross linkable polymeric composition is present in an amount between approximately 35 and 65% by weight.

10 10. A polymeric article according to any one of claims 1 to 9 wherein the article has a weight of from approximately 20 to 2000 g/m².

11. A polymeric article according to claim 10 wherein the article has a weight of from approximately 100 to 1500 g/m².

12. A polymeric article according to claim 11 wherein the article has a
15 weight of from approximately 500 to 1000 g/m².

13. A polymeric article according to any one of claims 1 to 12 wherein the reinforcing web is selected from one or more of the group consisting of glass fibres; carbon and graphite fibres, polymeric fibres, boron filaments, ceramic fibres, metal fibres, asbestos fibres, beryllium fibres, silica fibres and silicon
20 carbide fibres.

14. A polymeric article according to claim 13 wherein the glass fibres are in the form of fibreglass sheets or matts.

15. A polymeric article according to any one of claims 1 to 14 wherein the UV curable polymeric resin is selected from the group consisting of a curable
25 polyester, a vinyl ester resin, a epoxy vinyl ester resin and a bisphenol- A epoxy resin.

16. A polymeric article according to any one of claims 1 to 15 wherein the photoinitiator is present in an amount of from 0.01% to 5% by weight.

17. A polymeric article according to claim 16 wherein the photoinitiator is present in an amount of from 0.1% to 0.2% by weight.

5 18. A polymeric article according to anyone of claims 1 to 17 wherein the photoinitiator is selected from the group consisting of Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-{4-(methylthio)phenyl}-2-morpholino-propanone-1), Merck Darocur 1664, Rohm
10 Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55 (55) (methyl phenyl glyoxylate phenyl ketone).

19. A polymeric article according to any one of claims 1 to 18 wherein the thermal initiator, if present, is selected from the group consisting of peroxides,
15 1,1-di-*tert*-butyl peroxy-3,3,5-trimethylcyclohexane, and sec-isopropyl percarbonate or a combination thereof.

20. A polymeric article according to any one of claims 1 to 19, wherein the cross-linkable polymeric composition further includes an additive or modifier selected from the group consisting of inhibitors, UV stabilisers, UV absorbers,
20 antioxidants, tinting agents, transfer agents, viscosity modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers, thixotropic agents, slip and blocking agents, and air release agents or a combination thereof.

21. A process for preparing a partially cured reinforced polymeric article
25 including:

providing one or more layers, each layer including:

a reinforcing web; and

an effective amount of a cross-linkable polymeric composition including:

- a UV curable polymeric resin and
- a photoinitiator; or
- 5 a photoinitiator and a thermal catalyst;

impregnating the reinforcing web with the cross-linkable polymeric composition; and

- exposing the impregnated web to a source of ultraviolet (UV) radiation for a period of less than approximately 120 seconds, at an intensity
- 10 sufficient to partially cure the resin.

22. A process according to claim 21 wherein the impregnated web is exposed to ultraviolet (UV) radiation for a period of from approximately 5 to 60 seconds.

- 23. A process according to claim 22 wherein the impregnated web is
- 15 exposed to ultraviolet (UV) radiation for a period of from 10 to 45 seconds.

24. A process according to any one of claims 21 to 23 wherein the intensity of the ultraviolet (UV) radiation is from approximately 1×10^{-5} to 10×10^{-7} W/cm².

- 25. A process according to claim 24 wherein the intensity of the
- 20 ultraviolet (UV) radiation is from approximately 5×10^{-5} and 5×10^{-6} W/cm².

26. A process according to any one of claims 21 to 25 wherein the polymeric article includes two or more layers, and the layers are of substantially the same thickness.

- 27. A process according to any one of claims 21 to 25 wherein the
- 25 polymeric article includes two or more layers, and one or more of the layers is of differing thickness from one other layer in the article.

28. A process according to any one of claims 21 to 27 wherein the polymeric article includes two or more layers, and one or more of the layers includes a reinforcing web of differing material from the material of one other layer in the article.

5 29. A process according to any one of claims 21 to 25 wherein the reinforcing web is selected from one or more of the group consisting of glass fibres; carbon and graphite fibres, polymeric fibres, boron filaments, ceramic fibres, metal fibres, asbestos fibres, beryllium fibres, silica fibres and silicon carbide fibres.

10 30. A process according to claim 29 wherein the glass fibres are in the form of fibreglass sheets or matts.

15 31. A process according to any one of claims 21 to 30 wherein the UV curable polymeric resin is selected from the group consisting of a curable polyester, a vinyl ester resin, a epoxy vinyl ester resin and a bisphenol- A epoxy resin.

32. A process according to any one of claims 21 to 31 wherein the photoinitiator is present in an amount of from 0.01% to 5% by weight.

33. A process according to claim 32 wherein the photoinitiator is present in an amount of from 0.1% to 0.2% by weight.

20 34. A process according to any one of claims 21 to 33 wherein the photoinitiator is selected from the group consisting of Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-{4-(methylthio)phenyl}-2-morpholino-propanone-1), Merck Darocur 1664, Rohm
25 Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55 (55) (methyl phenyl glyoxylate phenyl ketone).

35. A process according to any one of claims 21 to 34 wherein the thermal initiator, if present, is selected from the group consisting of peroxides, 1,1-di-*tert*-butyl peroxy-3,3,5-trimethylcyclohexane, and *sec*-isopropyl percarbonate or a combination thereof.

5 36. A process according to any one of claims 21 to 35 wherein the cross-linkable polymeric composition further includes an additive or modifier selected from the group consisting of inhibitors, UV stabilisers, UV absorbers, antioxidants, tinting agents, transfer agents, viscosity modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers,
10 thixotropic agents, slip and blocking agents, and air release agents or a combination thereof.

37. A laminate polymeric article including:

a partially cured reinforced polymeric article which includes one or more layers, each layer including:

15 a reinforcing web;

a partially cured cross-linkable polymeric composition formed from:

an ultraviolet (UV) curable polymeric resin; and

a photoinitiator; or

a photoinitiator and a thermal initiator;

20 wherein the polymeric resin and the photoinitiator are selected to permit formation of the partially cured cross-linkable polymeric composition in less than approximately 120 seconds; and

a first protective coating or film overlaying at least a portion of a surface of the reinforced polymeric article.

25 38. A laminate polymeric article according to claim 37 wherein the partially cured cross-linkable polymeric composition is formed in approximately 5 to 60 seconds.

39. A laminate polymeric article according to claim 38 wherein the partially cured cross-linkable polymeric composition is formed in approximately 10 to 45 seconds.

40. A laminate polymeric article according to any one of claims 37 to 39
5 wherein there are two or more layers and the layers are of substantially the same thickness.

41. A laminate polymeric article according to any one of claims 37 to 39 wherein there are two or more layers and one or more of the layers is of a differing thickness from one other layer in the article.

10 42. A laminate polymeric article according to any one of claims 37 to 41 wherein there are two or more layers and one or more of the layers includes a reinforcing web of differing material from the material of one other layer in the article.

15 43. A laminate polymeric article according to any one of claims 37 to 42 wherein the cross-linkable polymeric composition is present in an amount between approximately 10 and 90% by weight.

44. A laminate polymeric article according to claim 43 wherein the cross linkable polymeric composition is present in an amount between approximately 25 and 75% by weight.

20 45. A laminate polymeric article according to claim 44 wherein the cross linkable polymeric composition is present in an amount between approximately 35 and 65% by weight.

46. A laminate polymeric article according to any one of claims 1 to 45 wherein the article has a weight of from approximately 20 to 2000 g/m².

25 47. A laminate polymeric article according to claim 46 wherein the article has a weight of from approximately 100 to 1500 g/m².

48. A laminate polymeric article according to claim 47 wherein the article has a weight of from approximately 500 to 1000 g/m².

49. A laminate polymeric article according to any one of claims 37 to 48 wherein the partially cured reinforced polymeric article includes two or more layers
5 and the layers are of substantially the same thickness.

50. A laminate polymeric article according to any one of claims 37 to 48 wherein the partially cured reinforced polymeric article includes two or more layers and one or more layers is of differing thickness from one other layer in the article.

51. A laminate polymeric article according to any one of claims 37 to 50
10 wherein the partially cured reinforced polymeric article includes two or more layers and one or more layers includes a reinforcing web of differing material from the material of one other layer in the article.

52. A laminate polymeric article according to any one of claims 37 to 51
15 wherein the protective coating or layer is applied to one major surface of the polymeric article.

53. A laminate polymeric article according to any one of claims 37 to 51 wherein the protective coating or layer is applied to both major surfaces of the polymeric article.

54. A laminate polymeric article according to any one of claims 37 to 53
20 wherein the first protective coating or film is a polymeric film or sheet.

55. A laminate polymeric article according to claim 54 wherein the polymeric film or sheet is a thermoplastic polymeric film.

56. A laminate polymeric article according to claim 55 wherein the thermoplastic polymeric film is selected from the group consisting of polyethylene,
25 polypropylene or nylon film.

57. A laminate polymeric article according to any one of claims 37 to 56 wherein the first protective coating or film is UV opaque.

58. A laminate polymeric article according to any one of claims 37 to 57 further including a UV opaque outer coating overlaying, at least in part, an exposed surface of the partially cured reinforced polymeric article or first protective coating or film.

59. A laminate polymeric article according to claim 58 wherein the UV opaque outer coating is a metal foil.

60. A laminate polymeric article according to any one of claims 37 to 59 wherein the reinforcing web is selected from one or more of the group consisting of glass fibres; carbon and graphite fibres, polymeric fibres, boron filaments, ceramic fibres, metal fibres, asbestos fibres, beryllium fibres, silica fibres and silicon carbide fibres.

61. A laminate polymeric article according to claim 60 wherein the glass fibres are in the form of fibreglass sheets or matts.

62. A laminate polymeric article according to any one of claims 37 to 61 wherein the UV curable polymeric resin is selected from the group consisting of a curable polyester, a vinyl ester resin, a epoxy vinyl ester resin and a bisphenol-A epoxy resin.

63. A laminate polymeric article according to any one of claims 37 to 62 wherein the photoinitiator is present in an amount of from 0.01% to 5% by weight.

64. A laminate polymeric article according to claim 63 wherein the photoinitiator is present in an amount of from 0.1% to 0.2% by weight.

65. A laminate polymeric article according to any one of claims 37 to 64 wherein photoinitiator is selected from the group consisting of Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-(4-

(methylthio)phenyl]-2-morpholino-propanone-1), Merck Darocur 1664, Rohm Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55 (55) (methyl phenyl glyoxylate phenyl ketone).

- 5 66. A laminate polymeric article according to any one of claims 37 to 65 wherein the thermal initiator, if present, is selected from the group consisting of peroxides, 1,1-di-*tert*-butyl peroxy-3,3,5-trimethylcyclohexane, and *sec*-isopropyl percarbonate or a combination thereof.

- 10 67. A laminate polymeric article according to any one of claims 37 to 66 wherein the cross-linkable polymeric composition further includes an additive or modifier selected from the group consisting of inhibitors, UV stabilisers, UV absorbers, antioxidants, tinting agents, transfer agents, viscosity modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers, thixotropic agents, slip and blocking agents, and air release
15 agents or a combination thereof.

68. A process of forming a shaped article including:

shaping one or more partially cured reinforced polymeric articles which include one or more layers, each layer including:

- 20 a reinforcing web;
 a partially cured cross-linkable polymeric composition formed from:
 an ultraviolet (UV) curable polymeric resin; and
 a photoinitiator; or
 a photoinitiator and a thermal initiator;

- 25 wherein the polymeric resin and the photoinitiator are selected to permit formation of the partially cured cross-linkable polymeric composition in less than approximately 120 seconds;

shaping one or more partially cured reinforced polymeric articles into a desired form; and

subjecting the formed article to a final curing step.

69. A process according to claim 68 wherein the partially cured cross-
5 linkable polymeric composition is formed in approximately 5 to 60 seconds.

70. A process according to claim 69 wherein the partially cured cross-
linkable polymeric composition is formed in approximately 10 to 45 seconds.

71. A process according to any one of claims 68 to 70 wherein the
partially cured reinforced polymeric article includes two or more layers and the
10 layers are of substantially the same thickness.

72. A process according to any one of claims 68 to 70 wherein the
partially cured reinforced polymeric article includes two or more layers and one or
more layers is of differing thickness from one other layer in the article.

73. A process according to any one of claims 68 to 72 wherein the
15 partially cured reinforced polymeric article includes two or more layers and one or
more layers includes a reinforcing web of differing material from the material of
one other layer in the article.

74. A process according to any one of claims 68 to 73 wherein the final
curing step includes exposing the formed article to UV radiation.

20 75. A process according to any one of claims 68 to 74 wherein the final
curing step includes a method involving applying heat and pressure to the formed
articles.

76. A process according to claim 74 wherein the UV radiation has an
intensity of from approximately 1×10^{-4} to 1×10^{-6} W/cm².

25 77. A process according to claim 76 wherein the UV radiation has an
intensity of from approximately 5×10^{-4} and 5×10^{-5} W/cm².

78. A process according to any one of claims 74 to 77 wherein the formed article is exposed to UV radiation for a period of from approximately 0.5 to 120 minutes.

79. A process according to claim 78 wherein the formed article is
5 exposed to UV radiation for a period of from approximately 10 to 45 minutes.

80. A process according to claim 74 wherein the final curing step includes subjecting the formed article to a thermal curing.

81. A process according to claim 80 wherein the temperature of the thermal curing is between approximately 50 and 150°C.

10 82. A process according to claim 81 wherein the temperature of the thermal curing is between approximately 65 and 100°C.

83. A process according to claim 75 wherein the pressure applied during the final cure is between approximately 30 and 100 psi.

84. A process according to claim 83 wherein the pressure applied during
15 the final cure is between approximately 50 and 70 psi.

85. A process according to any one of claims 68 to 84 wherein the reinforcing web is selected from one or more of the group consisting of glass fibres; carbon and graphite fibres, polymeric fibres, boron filaments, ceramic fibres, metal fibres, asbestos fibres, beryllium fibres, silica fibres and silicon
20 carbide fibres.

86. A process according to claim 85 wherein the glass fibres are in the form of fibreglass sheets or matts.

87. A process according to any one of claims 68 to 86 wherein the UV curable polymeric resin is selected from the group consisting of a curable
25 polyester, a vinyl ester resin, a epoxy vinyl ester resin and a bisphenol- A epoxy resin.

88. A process according to any one of claims 68 to 87 wherein the photoinitiator is present in an amount of from 0.01% to 5% by weight.

89. A process according to claim 88 wherein the photoinitiator is present in an amount of from 0.1% to 0.2% by weight.

5 90. A process according to any one of claims 68 to 89 wherein the photoinitiator is selected from the group consisting of Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-{4-(methylthio)phenyl}-2-morpholino-propanone-1), Merck Darocur 1664, Rohm
10 Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55 (55) (methyl phenyl glyoxylate phenyl ketone).

91. A process according to any one of claims 68 to 90 wherein the thermal initiator, if present, is selected from the group consisting of peroxides, 1,1-
15 di-*tert*-butyl peroxy-3,3,5-trimethylcyclohexane, and *sec*-isopropyl percarbonate or a combination thereof.

92. A process according to any one of claims 68 to 91 wherein the cross-linkable polymeric composition further includes an additive or modifier selected from the group consisting of inhibitors, UV stabilisers, UV absorbers, antioxidants,
20 tinting agents, transfer agents, viscosity modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers, thixotropic agents, slip and blocking agents, and air release agents or a combination thereof.

93. A cured shaped article formed by a process according to any one of
25 claims 68 to 92.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2003/001617

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ⁷: C08J 5/24, C08F 2/48, 2/44, B29B 15/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08J 5/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT & JAPIO (Search terms: prepreg+, partial+ cur+, reinforc+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 352 782 B (YEAGER et al.) 5 March 2002 See Example 2 and column 14 lines 50-63.	1-93
X	US 6 207 726 B (OHTANI et al.) 27 March 2001 See column 5 lines 17-24, column 14 line 56 to column 15 line 46 and Examples 1-11	1-93
X	US 5 721 323 A (SCHULTZ et al.) 24 February 1998 See column 9 line 56 to column 10 line 54	1-93

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
29 January 2004

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 126 192 A (CHELLIS et al.) 30 June 1992 See Examples	1-93
X	US 4 623 578 A (MARCHETTI et al.) 18 November 1986 See column 5 line 53 to column 6 line 30 and Example 3	1-93
X	EP 0 441 453 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 14 August 1991 See page 5 lines 4-13 and Example 1	1-93
X	EP 0 248 248 B (INTERNATIONAL BUSINESS MACHINES CORPORATION) 7 August 1991 See whole document	1-93

INTERNATIONAL SEARCH REPORT

International application No.

Information on patent family members

PCT/AU2003/001617

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	6352782	CN	1468904	EP	1265946	EP	1378534
		US	2001053450	US	2001053820	US	2002028337
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US	5721323	AU	77211/91	BR	9102108	CA	2042858
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		CN	1136816	EP	0458502	EP	0729484
		FI	912435	IL	98185	JP	4227924
		JP	11310627	JP	2000136288	JP	2000309626
		JP	2002178342	NO	911933	PT	97724
		SG	43193	US	5169473	US	5308895
		US	5314720	US	5620789	WO	9512627
		ZA	9103801				
US	5126192	EP	0440918	JP	3222733		
US	4623578						
EP	0441453	CA	2034969	JP	4212834	US	5672311
EP	0248248	JP	62280003	US	4732636		
END OF ANNEX							